

## PATENT COOPERATION TREATY

097639.8

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents  
United States Patent and Trademark  
Office  
Box PCT  
Washington, D.C.20231  
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

<b>Date of mailing</b> (day/month/year) 25 April 2000 (25.04.00)	
<b>International application No.</b> PCT/JP99/04723	<b>Applicant's or agent's file reference</b> IJE9903PCT
<b>International filing date</b> (day/month/year) 31 August 1999 (31.08.99)	<b>Priority date</b> (day/month/year) 01 September 1998 (01.09.98)
<b>Applicant</b> SAKAGUCHI, Futoshi et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:

20 March 2000 (20.03.00)

☐ in a notice effecting later election filed with the International Bureau on:2. The election ☒ was☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

<p>The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland</p> <p>Facsimile No.: (41-22) 740.14.35</p>	<p>Authorized officer Kiwa Mpay</p> <p>Telephone No.: (41-22) 338.83.38</p>
--	---

PCT

# REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

receiving Office use only

International Application No.

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference  
(if desired) (12 characters maximum)

IJE9903PCT



## Box No. I TITLE OF INVENTION

HYDROCRACKING METHOD AND HYDROCRACKING CATALYST

## Box No. II APPLICANT

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

JAPAN ENERGY CORPORATION

10-1, Toranomom 2-chome, Minato-ku, Tokyo  
105-0001 JAPAN

☐ This person is also inventor.

Telephone No. 03-5573-6280

Facsimile No. 03-5573-6805

Teleprinter No.

State (that is, country) of nationality:

JAPAN

State (that is, country) of residence:

JAPAN

This person is applicant for the purposes of:

☐ all designated States

☒ all designated States except the United States of America

☐ the United States of America only

☐ the States indicated in the Supplemental Box

## Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

SAKAGUCHI Futoshi

c/o JAPAN ENERGY CORPORATION,  
17-35, Niizominami 3-chome, Toda-shi, Saitama  
335-8502 JAPAN

This person is:

☐ applicant only

☒ applicant and inventor

☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

JAPAN

State (that is, country) of residence:

JAPAN

This person is applicant for the purposes of:

☐ all designated States

☐ all designated States except the United States of America

☒ the United States of America only

☐ the States indicated in the Supplemental Box

☒ Further applicants and/or (further) inventors are indicated on a continuation sheet.

## Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:

☒ agent

☐ common representative

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

Patent Attorney KAWAKITA Kijuro(9979)

Shinjuku MM Building  
1-15, Shinjuku 5-chome, Shinjuku-ku, Tokyo  
160-0022 JAPAN

Telephone No.

03-5362-3180

Facsimile No.

03-3341-6103

Teleprinter No.

☐ Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

## Continuation of Box No. 11 FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

If none of the following sub-boxes is used, this sheet should not be included in the request.

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

TOGAWA Seiji

c/o JAPAN ENERGY CORPORATION,  
17-35, Niizominami 3-chome, Toda-shi, Saitama  
335-8502 JAPAN

This person is:

- ☐ applicant only  
☒ applicant and inventor  
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

JAPAN

State (that is, country) of residence:

JAPAN

This person is applicant for the purposes of:

☐ all designated States☐ all designated States except the United States of America☒ the United States of America only☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

ISHIDA Katsuaki

c/o JAPAN ENERGY CORPORATION,  
17-35, Niizominami 3-chome, Toda-shi, Saitama  
335-8502 JAPAN

This person is:

- ☐ applicant only  
☒ applicant and inventor  
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

JAPAN

State (that is, country) of residence:

JAPAN

This person is applicant for the purposes of:

☐ all designated States☐ all designated States except the United States of America☒ the United States of America only☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

KOBAYASHI Manabu

c/o JAPAN ENERGY CORPORATION,  
17-35, Niizominami 3-chome, Toda-shi, Saitama  
335-8502 JAPAN

This person is:

- ☐ applicant only  
☒ applicant and inventor  
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

JAPAN

State (that is, country) of residence:

JAPAN

This person is applicant for the purposes of:

☐ all designated States☐ all designated States except the United States of America☒ the United States of America only☐ the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

This person is:

- ☐ applicant only  
☐ applicant and inventor  
☐ inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:

State (that is, country) of residence:

This person is applicant for the purposes of:

☐ all designated States☐ all designated States except the United States of America☐ the United States of America only☐ the States indicated in the Supplemental Box☐ Further applicants and/or (further) inventors are indicated on another continuation sheet.

**Box No.V DESIGNATION OF STATES**

The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes; at least one must be marked):

**Regional Patent**

- ☐ **AP ARIPO Patent:** GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, SD Sudan, SL Sierra Leone, SZ Swaziland, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- ☐ **EA Eurasian Patent:** AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☒ **EP European Patent:** AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☐ **OA OAPI Patent:** BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)

**National Patent (if other kind of protection or treatment desired, specify on dotted line):**

- |  |  |
|--|--|
| <input type="checkbox"/> <b>AE</b> United Arab Emirates                  | <input type="checkbox"/> <b>LR</b> Liberia                                   |
| <input type="checkbox"/> <b>AL</b> Albania                               | <input type="checkbox"/> <b>LS</b> Lesotho                                   |
| <input type="checkbox"/> <b>AM</b> Armenia                               | <input type="checkbox"/> <b>LT</b> Lithuania                                 |
| <input type="checkbox"/> <b>AT</b> Austria                               | <input type="checkbox"/> <b>LU</b> Luxembourg                                |
| <input type="checkbox"/> <b>AU</b> Australia                             | <input type="checkbox"/> <b>LV</b> Latvia                                    |
| <input type="checkbox"/> <b>AZ</b> Azerbaijan                            | <input type="checkbox"/> <b>MD</b> Republic of Moldova                       |
| <input type="checkbox"/> <b>BA</b> Bosnia and Herzegovina                | <input type="checkbox"/> <b>MG</b> Madagascar                                |
| <input type="checkbox"/> <b>BB</b> Barbados                              | <input type="checkbox"/> <b>MK</b> The former Yugoslav Republic of Macedonia |
| <input type="checkbox"/> <b>BG</b> Bulgaria                              |  |
| <input type="checkbox"/> <b>BR</b> Brazil                                | <input type="checkbox"/> <b>MN</b> Mongolia                                  |
| <input type="checkbox"/> <b>BY</b> Belarus                               | <input type="checkbox"/> <b>MW</b> Malawi                                    |
| <input type="checkbox"/> <b>CA</b> Canada                                | <input type="checkbox"/> <b>MX</b> Mexico                                    |
| <input type="checkbox"/> <b>CH and LI</b> Switzerland and Liechtenstein  | <input type="checkbox"/> <b>NO</b> Norway                                    |
| <input type="checkbox"/> <b>CN</b> China                                 | <input type="checkbox"/> <b>NZ</b> New Zealand                               |
| <input type="checkbox"/> <b>CU</b> Cuba                                  | <input type="checkbox"/> <b>PL</b> Poland                                    |
| <input type="checkbox"/> <b>CZ</b> Czech Republic                        | <input type="checkbox"/> <b>PT</b> Portugal                                  |
| <input type="checkbox"/> <b>DE</b> Germany                               | <input type="checkbox"/> <b>RO</b> Romania                                   |
| <input type="checkbox"/> <b>DK</b> Denmark                               | <input type="checkbox"/> <b>RU</b> Russian Federation                        |
| <input type="checkbox"/> <b>EE</b> Estonia                               | <input type="checkbox"/> <b>SD</b> Sudan                                     |
| <input type="checkbox"/> <b>ES</b> Spain                                 | <input type="checkbox"/> <b>SE</b> Sweden                                    |
| <input type="checkbox"/> <b>FI</b> Finland                               | <input checked="" type="checkbox"/> <b>SG</b> Singapore                      |
| <input type="checkbox"/> <b>GB</b> United Kingdom                        | <input type="checkbox"/> <b>SI</b> Slovenia                                  |
| <input type="checkbox"/> <b>GD</b> Grenada                               | <input type="checkbox"/> <b>SK</b> Slovakia                                  |
| <input type="checkbox"/> <b>GE</b> Georgia                               | <input type="checkbox"/> <b>SL</b> Sierra Leone                              |
| <input type="checkbox"/> <b>GH</b> Ghana                                 | <input type="checkbox"/> <b>TJ</b> Tajikistan                                |
| <input type="checkbox"/> <b>GM</b> Gambia                                | <input type="checkbox"/> <b>TM</b> Turkmenistan                              |
| <input type="checkbox"/> <b>HR</b> Croatia                               | <input type="checkbox"/> <b>TR</b> Turkey                                    |
| <input type="checkbox"/> <b>HU</b> Hungary                               | <input type="checkbox"/> <b>TT</b> Trinidad and Tobago                       |
| <input checked="" type="checkbox"/> <b>ID</b> Indonesia                  | <input type="checkbox"/> <b>UA</b> Ukraine                                   |
| <input type="checkbox"/> <b>IL</b> Israel                                | <input type="checkbox"/> <b>UG</b> Uganda                                    |
| <input type="checkbox"/> <b>IN</b> India                                 | <input checked="" type="checkbox"/> <b>US</b> United States of America       |
| <input type="checkbox"/> <b>IS</b> Iceland                               |  |
| <input checked="" type="checkbox"/> <b>JP</b> Japan                      | <input type="checkbox"/> <b>UZ</b> Uzbekistan                                |
| <input type="checkbox"/> <b>KE</b> Kenya                                 | <input type="checkbox"/> <b>VN</b> Viet Nam                                  |
| <input type="checkbox"/> <b>KG</b> Kyrgyzstan                            | <input type="checkbox"/> <b>YU</b> Yugoslavia                                |
| <input type="checkbox"/> <b>KP</b> Democratic People's Republic of Korea | <input type="checkbox"/> <b>ZA</b> South Africa                              |
|  | <input type="checkbox"/> <b>ZW</b> Zimbabwe                                  |
| <input checked="" type="checkbox"/> <b>KR</b> Republic of Korea          |  |
| <input type="checkbox"/> <b>KZ</b> Kazakhstan                            |  |
| <input type="checkbox"/> <b>LC</b> Saint Lucia                           |  |
| <input type="checkbox"/> <b>LK</b> Sri Lanka                             |  |

Check-boxes reserved for designating States which have become party to the PCT after issuance of this sheet:

**Precautionary Designation Statement:** In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation of a designation consists of the filing of a notice specifying that designation and the payment of the designation and confirmation fees. Confirmation must reach the receiving Office within the 15-month time limit.)

<b>Box No. VI PRIORITY CLAIM</b>		<input type="checkbox"/> Further priority claims are indicated in the Supplemental Box.		
Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application: * regional Office	international application: receiving Office
item (1) 01.09.98	Patent Application 10-246459	JAPAN		
item (2)				
item (3)				

☒ The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as item(s): (1)

\* Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(ii)). See Supplemental Box.

**Box No. VII INTERNATIONAL SEARCHING AUTHORITY**

**Choice of International Searching Authority (ISA)**  
(if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):

ISA / EP

**Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):**

Date (day/month/year)

Number

Country (or regional Office)

**Box No. VIII CHECK LIST; LANGUAGE OF FILING**

This international application contains the following number of sheets:

request : 4  
description (excluding sequence listing part) : 20  
claims : 4  
abstract : 1  
drawings : 3  
sequence listing part of description :  
Total number of sheets : 32

This international application is accompanied by the item(s) marked below:

1. ☒ fee calculation sheet
2. ☒ separate signed power of attorney
3. ☐ copy of general power of attorney, reference number, if any:
4. ☐ statement explaining lack of signature
5. ☐ priority document(s) identified in Box No. VI as item(s):
6. ☐ translation of international application into (language):
7. ☐ separate indications concerning deposited microorganism or other biological material
8. ☐ nucleotide and/or amino acid sequence listing in computer readable form
9. ☒ other (specify): REQUEST FOR TRANSMITTAL OF PRIORITY DOCUMENT

Figure of the drawings which should accompany the abstract:

Fig. 3

Language of filing of the international application:

English

**Box No. IX SIGNATURE OF APPLICANT OR AGENT**

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

  
KAWAKITA Kijuro

For receiving Office use only

1. Date of actual receipt of the purported international application:	2. Drawings:  <input type="checkbox"/> received:  <input type="checkbox"/> not received:
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:	
4. Date of timely receipt of the required corrections under PCT Article 11(2):	
5. International Searching Authority (if two or more are competent): ISA /	6. <input type="checkbox"/> Transmittal of search copy delayed until search fee is paid.

For International Bureau use only

Date of receipt of the record copy by the International Bureau:

REC'D 07 DEC 2000

WIPO

PCT

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)


Applicant's or agent's file reference IJE9903PCT	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/JP99/04723	International filing date (day/month/year) 31/08/1999	Priority date (day/month/year) 01/09/1998
International Patent Classification (IPC) or national classification and IPC C10G47/12		
Applicant JAPAN ENERGY CORPORATION et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 7 sheets, including this cover sheet.  
  
☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 4 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand  20/03/2000	Date of completion of this report  04.12.2000
Name and mailing address of the international preliminary examining authority:   European Patent Office D-80293 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer  de Cauwer, R  Telephone No. +49 89 2399 7344



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/JP99/04723

**I. Basis of the report**

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).)*:

**Description, pages:**

1-20 as originally filed

**Claims, No.:**

1-14 with telefax of 08/09/2000

**Drawings, sheets:**

1/3-3/3 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/JP99/04723

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):  
*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes:	Claims	
	No:	Claims	1-14
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-14
Industrial applicability (IA)	Yes:	Claims	1-14
	No:	Claims	

2. Citations and explanations  
**see separate sheet**

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:  
**see separate sheet**

**Re Item V**

**Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

Novelty - claim 1

Claim 1 is a claim for a method of hydrocracking hydrocarbon oils with a 10 % distillation temperature of 300°C or higher, comprising the steps of: precontacting the hydrocracking catalyst with an organic nitrogen compound; and contacting a feed oil substantially comprised of hydrocarbon oils and hydrogen with the hydrocracking catalyst that has been contacted with the organic nitrogen compound in order to obtain a hydrocarbon oil with a lower boiling point than that of the feed oil; the hydrocracking catalyst consisting of W, Mo, Ni and Co, on a carrier made from a porous refractory oxide, the organic nitrogen compound being an organic nitrogen compound having a boiling point that is lower than a 50% distillation temperature of the feed oil and that is higher than 200°C.

The following prior art documents are considered to be relevant:

D4: FR-A-2 668 951 (INST FRANCAIS DU PETROL) 15 May 1992 (1992-05-15)

The document D4 discloses a catalyst that can be used for hydrocracking hydrocarbon oils with a 10% distillation temperature of 300 °C or higher (p 11, table 1 & p 12), being passivated with a basic nitrogen containing compound (p 5, line 20-30 & p 7, line 3-15), like thiourea, quaternary ammonium components, etc (p 7, line 3-14), prior to exposing the catalyst to the feedstock (p 8, line 16-19), containing a hydrogenation active metal selected from Ni, Mo or W on a support of alumina or mixed silicium-alumina (p 2, line 19-23) to obtain lighter and more valuable products .

Thus, the subject-matter of claim 1 lacks novelty over D4 (Article 33 (2) PCT).

Novelty - claim 2 - 11

D4 further discloses that the feed can be gas oil (p 1, line 12) ; the step of sulfiding and contacting the catalyst with a nitrogen compound occur simultaneously (p6, line 12-30)

; the catalyst may be passivated in-situ by mixing a suitable passivating agent with the initial feedstock to be contacted with the catalyst (p 5, line 23-27), that the passivating petroleum fraction contains 0.015 wt% nitrogen (p 12, table 2), that the hydrocracking catalyst contains 0.05 to 10 wt% of nitrogen ; that the passivating petroleum fraction is kerosene (p 6, line 11).

For these reasons and because claims 2 - 11 are dependent on claim 1, which does not meet the requirements of Article 33 (2) PCT, they too do not meet the requirements of the PCT with respect to novelty.

Inventive step - claims 1 - 11

Since D4 is concerned with the same technical problems as the application, notably the provision of a catalyst which is resistant to deactivation by nitrogen compounds, no inventive step can be recognized (Article 33 (3) PCT).

Novelty - claim 12

The applicant should note that the expression "which is used for hydrocracking a feed oil derived from petroleum by contacting the feed oil and hydrogen with the hydrocracking catalyst to obtain a hydrocarbon oil with a boiling point lower than that of the feed oil" is only an indication of an intended use which cannot limit the claimed subject-matter.

Furthermore, it should be noted that a catalyst cannot be defined in terms of the boiling point of a feed, this renders the claim unclear (Article 6 PCT), as the feed is not necessarily present.

Thus, claim 12 is a product claim for a hydrocracking catalyst, comprising: a carrier made from a porous oxide; a hydrogenation active metal component, and an organic nitrogen compound with a boiling point that is higher than 200 °C, the content of the organic nitrogen compound being not less than 0.01 wt% by nitrogen weight per the hydrogenation catalyst.

However, all the technical features of claim 12 are already disclosed in D4 (see reasoning claim 1, the content of nitrogen in the catalyst varies from 0.05 to 10 wt% (p 9, line 13-14)).

Therefore, claim 12 does not meet the requirements of Article 33 (2) PCT.

Novelty - claims 13 - 14

Since claims 13 - 14 are dependent on claim 12, which does not meet the requirements of Article 33 (2) PCT, they too do not meet the requirements of the PCT with respect to novelty.

Inventive step - claims 12 - 14

Since D4 is concerned with the same technical problems as the application, notably to provide a hydrocracking method and a hydrocracking catalyst used by this method with which the initial deactivation rate of the hydrocracking catalyst is slowed and the middle distillate yield is improved and the activity following initial deactivation is improved, and solves the problem in the same way, notably the passivation of the catalyst with a nitrogen compound boiling above 200°C, prior to hydrocracking, no inventive step can be recognized (Article 33 (3) PCT).

### **Re Item VIII**

#### **Certain observations on the international application**

Claim 2 is drafted as an independent claim, relating to "a method of hydrocracking hydrocarbon oils derived from petroleum, ...", but it is in fact concerned with the same scope as claim 1, relating to "a method of hydrocracking hydrocarbon oils ...". Thus claims 1 and 2 lack conciseness.

It would therefore appear more appropriate if claim 2 were drafted as a dependent claim to claim 1 (Rule 6.4 (a) & (b)).

In claim 12 the expression "which is used for hydrocracking a feed oil derived from petroleum by contacting the feed oil and hydrogen with the hydrocracking catalyst to obtain a hydrocarbon oil with a boiling point lower than that of the feed oil" is only an indication of an intended use and therefore does not limit the claimed subject-matter.

The hydrocracking catalyst claimed in claim 12 is defined in terms of feed

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

---

International application No. PCT/JP99/04723

characteristics (..an organic nitrogen compound with a boiling point that is lower than the 50% distillation temperature of the feed oil...). This cannot be a limiting feature as the catalyst is independent of the feed. Thus, claim 12 does not meet the requirements of Article 6 PCT.

Claim 14 lacks clarity because it is defined in terms of a desired result ("which is produced by contacting ... with the catalyst"). Thus claim 14 does not meet the requirements of Article 6 PCT.

## CLAIMS

1. A method of hydrocracking hydrocarbon oils with a 10% distillation temperature of 300 °C or higher, comprising the steps of:

pre-contacting a hydrocracking catalyst with an organic nitrogen compound; and

contacting a feed oil substantially comprised of hydrocarbon oils and hydrogen with the hydrocracking catalyst that has been contacted with the organic nitrogen compound in order to obtain a hydrocarbon oil with a lower boiling point than that of the feed oil;

the hydrocracking catalyst having a hydrogenation active metal component, that is selected from a group consisting of tungsten, molybdenum, nickel and cobalt, on a carrier made from a porous refractory oxide, and

the organic nitrogen compound being an organic nitrogen compound having a boiling point that is lower than a 50% distillation temperature of the feed oil and that is higher than 200°C.

2. A method of hydrocracking hydrocarbon oils with a 10% distillation temperature of 300 °C or higher derived from petroleum comprising the steps of:

contacting a petroleum fraction containing an organic nitrogen compound and having a 95% distillation temperature that is lower than the 50% distillation temperature of a feed oil substantially comprised

of hydrocarbon oils and that is higher than  $100^{\circ}\text{C}$  with a hydrocracking catalyst; and

contacting the feed oil and hydrogen with the hydrocracking catalyst that has been contacted with the petroleum fraction in order to obtain a hydrocarbon oil with a boiling point lower than that of the feed oil;

the hydrocracking catalyst having a hydrogenation active metal component, that is selected from a group consisting of tungsten, molybdenum, nickel and cobalt, on a carrier made from a porous refractory oxide.

3. The hydrocracking method according to Claim 1, further comprising a step of sulfiding the hydrocracking catalyst, wherein the step of contacting the organic nitrogen compound with hydrocracking catalyst and the step of sulfiding the hydrocracking catalyst are performed simultaneously.

4. The hydrocracking method according to Claim 2, further comprising a step of sulfiding the hydrocracking catalyst, wherein the step of contacting petroleum fraction with hydrocracking catalyst and the step of sulfiding the hydrocracking catalyst are performed simultaneously.

5. The hydrocracking method according to Claim 2, wherein the petroleum fraction comprises at least 2 ppm of the organic nitrogen

compound by nitrogen weight.

6. The hydrocracking method according to Claim 1 or Claim 3, wherein, as a result of contacting the organic nitrogen compound with hydrocracking catalyst, the hydrocracking catalyst comprises 0.01% to 1% by nitrogen weight of the organic nitrogen compound per catalyst weight.

7. The hydrocracking method according to any one of Claims 2, 4, and 5, wherein, as a result of contacting the petroleum fraction with hydrocracking catalyst, the hydrocracking catalyst contains 0.01% to 1% by nitrogen weight of the organic nitrogen compound per catalyst weight.

8. The hydrocracking method according to Claim 1 or 2, wherein a catalyst deactivation inhibitor is added when the feed oil and hydrogen are contacted with the hydrocracking catalyst.

9. The hydrocracking method according to Claim 8, wherein the catalyst deactivation inhibitor is a nitrogen compound.

10. The hydrocracking method according to Claim 9, wherein the inhibitor is added 5 ppm or less by weight of nitrogen with respect to the weight of the feed oil.

11. The hydrocracking method according to any one of Claims

2, 4 and 5, wherein the petroleum fraction is gas oil.

12. A hydrocracking catalyst, which is used for hydrocracking a feed oil with a 10% distillation temperature of 300 °C or higher derived from petroleum by contacting the feed oil and hydrogen with the hydrocracking catalyst to obtain a hydrocarbon oil with a boiling point lower than that of the feed oil, comprising:

a carrier made from a porous refractory oxide;

a hydrogenation active metal component that is selected from a group consisting of tungsten, molybdenum, nickel and cobalt, and

an organic nitrogen compound with a boiling point that is lower than the 50% distillation temperature of the feed oil and that is higher than 200°C,

the content of the organic nitrogen compound being not less than 0.01 wt% by nitrogen weight with respect to the weight of the hydrocracking catalyst.

13. The hydrocracking catalyst according to Claim 12, wherein the organic compound is an organic compound contained in gas oil or kerosene.

14. The hydrocracking catalyst according to Claim 12 or Claim 13, which is produced by contacting a solution of sulfiding agent dissolved in gas oil or kerosene with the catalyst having the carrier and the hydrogenation active metal component.

## PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>IJE9903PCT</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/JP 99/ 04723</b>	International filing date (day/month/year) <b>31/08/1999</b>	(Earliest) Priority Date (day/month/year) <b>01/09/1998</b>
Applicant <b>JAPAN ENERGY CORPORATION et al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

## 1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☐ the text is approved as submitted by the applicant.

☒ the text has been established by this Authority to read as follows:

**HYDROCRACKING METHOD AND CATALYST**

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☒ None of the figures.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 99/04723

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10G47/12 B01J37/20

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10G B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 668 951 A (INST FRANCAIS DU PETROL) 15 May 1992 (1992-05-15) abstract page 5, line 20 -page 7, line 15; claims 1-21; examples 1-9; tables 1,2 ---	1-14
X	US 5 366 615 A (BEZMAN RICHARD D) 22 November 1994 (1994-11-22) cited in the application column 4, line 69 -column 5, line 2 column 5, line 35 - line 38 ---	1-13
X	US 5 141 909 A (BEZMAN RICHARD D) 25 August 1992 (1992-08-25) cited in the application column 4, line 62 - line 64; claims 1,8,13,15 --- -/--	1-13

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

26 November 1999

Date of mailing of the international search report

07/12/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Michiels, P

# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/JP 99/04723

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>EP 0 335 754 A (EURECAT EUROP RETRAIT CATALYS) 4 October 1989 (1989-10-04) the whole document</p> <p>-----</p>	1-14

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 99/04723

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
FR 2668951	A	15-05-1992	NONE	
US 5366615	A	22-11-1994	US 5141909 A	25-08-1992
			CA 2057496 A	23-07-1992
			EP 0521116 A	07-01-1993
			JP 4313346 A	05-11-1992
			WO 9213046 A	06-08-1992
US 5141909	A	25-08-1992	CA 2057496 A	23-07-1992
			EP 0521116 A	07-01-1993
			JP 4313346 A	05-11-1992
			WO 9213046 A	06-08-1992
			US 5366615 A	22-11-1994
EP 0335754	A	04-10-1989	FR 2629368 A	06-10-1989
			AT 64555 T	15-07-1991
			CA 1340302 A	05-01-1999
			JP 1310739 A	14-12-1989
			JP 2840752 B	24-12-1998
			US 4977117 A	11-12-1990

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>7</sup> :</b> <b>C10G 47/12, B01J 37/20</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/12653</b> <b>(43) International Publication Date:</b> 9 March 2000 (09.03.00)
<b>(21) International Application Number:</b> PCT/JP99/04723 <b>(22) International Filing Date:</b> 31 August 1999 (31.08.99) <b>(30) Priority Data:</b> 10/246459 1 September 1998 (01.09.98) JP <i>01 Mar 01 / 30 Nov</i> <b>(71) Applicant (for all designated States except US):</b> JAPAN ENERGY CORPORATION [JP/JP]; 10-1, Toranomon 2-chome, Minato-ku, Tokyo 105-0001 (JP). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> SAKAGUCHI, Futoshi [JP/JP]; Japan Energy Corporation, 17-35, Niizominami 3-chome, Toda-shi, Saitama 335-8502 (JP); TOGAWA, Seiji [JP/JP]; Japan Energy Corporation, 17-35, Niizominami 3-chome, Toda-shi, Saitama 335-8502 (JP); ISHIDA, Katsuaki [JP/JP]; Japan Energy Corporation, 17-35, Niizominami 3-chome, Toda-shi, Saitama 335-8502 (JP); KOBAYASHI, Manabu [JP/JP]; Japan Energy Corporation, 17-35, Niizominami 3-chome, Toda-shi, Saitama 335-8502 (JP). <b>(74) Agent:</b> KAWAKITA, Kijuro; Shinjuku MM Building, 1-15, Shinjuku 5-chome, Shinjuku-ku, Tokyo 160-0022 (JP).		<b>(81) Designated States:</b> ID, JP, KR, SG, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> HYDROCRACKING METHOD AND CATALYST.  <b>(57) Abstract</b> <p>An organic nitrogen compound with a boiling point lower than a 50 % distillation temperature of feed oil is contacted with hydrocracking catalyst as pre-treatment. The hydrocracking catalyst is contacted with the feed oil and hydrogen to perform hydrocracking and obtain a hydrocarbon with a boiling point lower than the feed oil. Moreover, pre-treatment can also be performed by contacting hydrocracking catalyst with a petroleum fraction that has a 95 % distillation temperature lower than the 50 % distillation temperature of the feed oil and that contains organic nitrogen compound. As a result, the initial deactivation rate of the hydrocracking catalyst can be slowed and the middle distillate yield can be improved, and further, activity after initial deactivation can be improved.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## DESCRIPTION

## HYDROCRACKING METHOD AND CATALYST

## TECHNICAL FIELD

The present invention relates to a hydrocracking method for cracking feed oil, such as petroleum oil, and a hydrocracking catalyst used in this method, and in particular, the present invention relates to pre-treatment that is performed before cracking the feed oil and hydrocracking catalyst that has been pre-treated.

## BACKGROUND OF ART

Attention has recently been focused on hydrocracking as a method of cracking heavy oils to obtain light oils. This is because not only gasoline, but also middle distillate products, such as kerosene and gas oil, etc., are obtained by hydrocracking and their yields can be changed by changing operating conditions, and because quality of the product oil is the high quality that is suitable for the environment.

Two-stage hydrocracking is one known method of hydrocracking. Two-stage hydrocracking is conducted using, for instance, a two-stage hydrocracking system such as shown in Fig. 4. By means of this method, hydrogen and feed oil are fed to

first-stage reactor (or hydrorefining area) 41 loaded with hydrocracking catalyst and the feed oil is hydrocracked here. Hydrorefining is simultaneously performed with hydrocracking of the feed oil to pre-remove the nitrogen compounds, which are poisons of the hydrocracking catalyst loaded in second reactor 45. The outlet oil emitted from first-stage reactor 41 is sent to distillation tower 43 and the light fraction is distilled off here, while some of the heavy oil that remains is recycled to second-stage reactor 45. The nitrogen content of the heavy oil that is recycled to the hydrocracking catalyst in second-stage reactor 45 is less than 100 ppm. The product oil that has been hydrocracked at second-stage reactor 45 is again sent to distillation column 43 together with the outlet oil of first-stage reactor 41.

The hydrocracking catalyst used by second-stage reactor 45 of two-stage hydrocracking is usually pre-sulfided in the gas phase by introducing sulfiding agent to the hydrogen gas prior to starting the hydrocracking operation. Therefore, (the acid sites on) the catalyst loaded in second-stage reactor 45 will not be poisoned by nitrogen while pre-sulfiding is being performed.

Nevertheless, although the catalyst loaded in second-stage reactor 45 initially has high activity, once the hydrocracking operation is started, it becomes poisoned by the nitrogen contained in the nitrogen compound in the recycle oil and

deactivation quickly occurs. Moreover, once the large volumes of nitrogen compounds, such as the polycyclic aromatics and the compounds whose side chain is attached to carbazole in the recycle oil are adsorbed on the acid sites on the catalyst, they cause coke deactivation and as a result, the active sites around the acid sites that have adsorbed nitrogen compounds are poisoned, leading to a reduction in activity following initial deactivation.

Therefore, there is technology for preventing this deactivation of hydrocracking catalysts whereby the catalyst is pre-treated with ammonia either before the hydrocracking operation or at the beginning of hydrocracking. This technology is disclosed in US Patents No. 3,117,075, No. 3,778,365, No. 5,141,909, and No. 5,366,615. Moreover, technology is also known whereby a nitrogen compound, such as a basic nitrogen compound, and ammonia are added to hydrorefined recycle oil to treat the catalyst during the hydrocracking operation. This technology is disclosed in US Patents No. 3,213,013, No. 3,404,085, No. 3,505,208, and No. 3,816,296.

Nevertheless, according to the research of the inventors, it is difficult to retain catalyst deactivation inhibiting effect for a long enough period of time by the method whereby catalyst is treated using ammonia either before the hydrocracking operation or at the beginning of the operation. Moreover,

because hydrorefining readily occurs with the treatment using a nitrogen compound having a low boiling point, such as butyl amine, etc., disclosed in US Patent No. 3,213,013, catalyst deactivation inhibiting effect is not retained for a long enough period of time. Moreover, it is necessary to add relatively large volumes of conventional additives, with the amount of nitrogen compound added per feed oil being 5 to 200 ppm (nitrogen concentration).

#### DISCLOSURE OF THE INVENTION

The present invention solves the above-mentioned problems of background art, its object being to provide a hydrocracking method and a hydrocracking catalyst used by this method with which the initial deactivation rate of the hydrocracking catalyst is slowed and the middle distillate yield is improved and further, activity following initial deactivation is improved.

In accordance with the first aspect of the present invention, a method of hydrocracking hydrocarbon oils is provided, which comprises the steps of:

pre-contacting a hydrocracking catalyst with an organic nitrogen compound; and

contacting a feed oil substantially comprised of hydrocarbon oils and hydrogen with the hydrocracking catalyst that has been

contacted with the organic nitrogen compound in order to obtain a hydrocarbon oil with a lower boiling point than the feed oil;

the organic nitrogen compound being an organic nitrogen compound having a boiling point that is lower than a 50% distillation temperature of the feed oil and that is higher than 200°C.

The inventors discovered that covering (poisoning) the acid points of a hydrocracking catalyst with an organic nitrogen compound having appropriate adsorbing power and appropriate molecular size is effective for i) slowing the initial deactivation rate of the hydrocracking catalyst, ii) improving the middle distillate yield, and iii) improving activity following initial deactivation. The organic nitrogen compound used by the present invention is an organic nitrogen compound a boiling point that is lower than the 50% distillation temperature of the feed oil and that is higher than 200°C. It has a boiling point lower than the 50% distillation temperature of the feed oil because organic nitrogen compounds having too large molecular size should be removed. An organic nitrogen compound with a boiling point that is lower than (50% distillation temperature (°C))  $\times 0.9$  is further preferred. Moreover, the organic compound must have a boiling point higher than 200°C for the following reason. That is, it appears that an organic nitrogen compound with a boiling point of 200°C or lower cannot sufficiently cover

(be adsorbed on) the acid sites on a catalyst that is readily decomposed by hydrocracking for long periods of time. Moreover, if the organic nitrogen compound has a boiling point of 200°C or lower, molecular size is also relatively small and it cannot sufficiently cover the acid sites, and the compound is likely to relatively easily desorbed from the acid sites.

According to the method of the present invention, the above-mentioned organic nitrogen compound is contacted by hydrocracking catalyst prior to starting the hydrocracking operation. In contrast to the methods described in the above-mentioned published document, the organic nitrogen compound specified by the present invention is contacted with catalyst prior to the hydrocracking operation, not during the operation. Thus, a specific nitrogen compound is pre-contacted with catalyst prior to the hydrocracking operation so that the acid sites of the catalyst are covered by the organic nitrogen compound and therefore, even a very small amount of organic nitrogen compound is effective for long-term prevention of catalyst deactivation. For instance, the amount of organic nitrogen absorbed on a catalyst can be kept at 0.01% to 1% in terms of nitrogen weight per catalyst.

The method of the present invention further may comprise the step of sulfiding the above-mentioned hydrogenation catalyst and it is preferred that treatment whereby the above-mentioned

organic nitrogen compound is contacted with hydrocracking catalyst be performed simultaneously with the sulfiding treatment. When tert-butyl amine (b.p.: 44°C), which has been conventionally used, is mixed with gas oil in which carbon sulfide ( $\text{CS}_2$ ) for sulfiding treatment has been dissolved, a white precipitate forms, but a white precipitate does not form when the organic nitrogen compound having a boiling point of 200°C or higher in accordance with the present invention, such as tributyl amine (b.p.: 217°C), is mixed with gas oil. Therefore, pretreatment with the organic nitrogen compound is simultaneously performed with sulfiding treatment and as a result, the process can be simplified and the time needed for the entire process can be curtailed.

In accordance with the second aspect of the present invention, a method of hydrocracking hydrocarbon oils derived from petroleum is provided, which comprises the steps of:

contacting a petroleum fraction containing an organic nitrogen compound and having a 95% distillation temperature that is lower than the 50% distillation temperature of a feed oil substantially comprised of hydrocarbon oils and that is higher than 200°C with a hydrocracking catalyst; and

contacting the feed oil and hydrogen with the hydrocracking catalyst that has been contacted with the petroleum fraction in

order to obtain a hydrocarbon oil with a boiling point lower than the feed oil.

As with the first method, according to the hydrocracking method of this embodiment, it is possible to i) slow the initial deactivation rate of the hydrocracking catalyst, ii) improve the middle distillate yield, and iii) improve activity following initial deactivation. The petroleum fraction with a 95% distillation temperature that is lower than the 50% distillation temperature of the feed oil and that is higher than 200°C includes, for instance, gas oil and kerosene. The boiling point of gas oil is 220°C to 380°C and the boiling point of kerosene is 140°C to 250°C. Organic nitrogen compounds, such as aniline, pyridine, quinoline, indole, carbazole, and their derivatives, etc., are contained in the petroleum fraction used in the present invention. It appears that because these organic nitrogen compounds are contained in the petroleum fraction with a 95% distillation temperature higher than 200°C, the acid sites on the catalyst can be protected for a long period of time during the hydrocracking process. In order to perform the method of this embodiment, the hydrocracking catalyst should be pre-treated by being brought into contact with, for instance, gas oil or kerosene. The gas oil can be straight run gas oil, coker gas oil, gas oil obtained from desulfurization of vacuum gas oil,

their mixtures, gas oil obtained by hydrotreating these examples, etc.

In accordance with the third aspect of the present invention, a hydrocracking catalyst, which is used for hydrocracking a feed oil derived from petroleum by contacting the feed oil and hydrogen with the hydrocracking catalyst to obtain a hydrocarbon oil with a boiling point lower than that of the feed oil, is provided. The hydrocracking catalyst comprises:

- a carrier made from a porous refractory oxide;

- a hydrogenation active metal component; and

- an organic nitrogen compound with a boiling point that is lower than the 50% distillation temperature of the feed oil and that is higher than 200°C; the content of the organic nitrogen compound being not less than 0.01 wt% by nitrogen weight per the hydrogenation catalyst.

It is preferred that the hydrocracking catalyst does not contain organic compound having a boiling point exceeding the 50% distillation temperature of the feed oil because organic nitrogen compounds having too large molecular size should be removed.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows the process flow of a hydrocracking system capable of performing the hydrocracking method of the present invention.

Fig. 2 shows the process flow of a different hydrocracking system capable of performing the hydrocracking method of the present invention.

Fig. 3 shows the process flow of a different hydrocracking system capable of performing the hydrocracking method of the present invention that is equipped with a recycle system.

Fig. 4 shows the process flow of a two-stage hydrocracking system capable of performing the hydrocracking method of the present invention.

Fig. 5 shows the process flow of a series flow-type hydrocracking system capable of performing the hydrocracking method of the present invention.

#### BEST MODE FOR CARRYING OUT THE INVENTION

The feed oil that serves as the starting material of the hydrocracking process of the present invention is usually feed oil with a 10% distillation temperature of 200°C or higher, preferably a 10% distillation temperature of 300°C or higher. There are no special restrictions to the feed oil, but feed oil derived from crude oil, coal liquefaction oil, oil shell, oil sand, etc., and Fischer-Tropsch synthetic oil, etc., are preferably used. The hydrocracking method and catalyst of the present invention is particularly effective for feed oil that has been hydrorefined to a nitrogen content of 100 ppm or less,

preferably 10 ppm or less, particularly 2 ppm or less. Such hydrorefined feed oil is, for instance, feed oil that has passed through the first stage of hydrocracking of two-stage hydrocracking.

Typical examples of the flow process of hydrocracking systems capable of using the hydrocracking method of the present invention are shown in Figs. 1 to 5. The system shown in Fig. 1 uses a reactor in only 1 stage, but the system in Fig. 2 uses reactors in two stages. The systems in Figs. 3 to 5 each have a recycle path from the distillation tower to the reactor. By means of the system in Fig. 4, once hydrocracking of feed oil has been performed by first-stage reactor 41, the oil is sent to distillation tower 43 and the light oil is recovered, while the remaining heavy oil is sent to second-stage reactor 45. After hydrocracking in second-stage reactor 45, the oil is again sent to distillation tower 43. By means of the system shown in Fig. 5, the first-stage reactor, second-stage reactor, and distillation tower are connected in this order and the heavy oil from the distillation tower is recycled to the second-stage reactor. By means of the systems in Figs. 4 and 5, hydrorefining is performed at once with the first-stage reactor and therefore, these systems are suitable for the hydrocracking method of the present invention. Consequently, the hydrocracking catalyst of the present invention is suitable as the catalyst used by the

second-stage reactor of a two-stage or a multi-stage hydrocracking system, such as shown in Figs. 4 and 5.

Nevertheless, the present invention can also be used for hydrocracking by the process flow in Figs. 1 and 2 using fraction that has been hydrorefined at least once as the starting material.

The hydrocracking of the present invention is a process whereby fractions corresponding to kerosene, gas oil, etc., that are lighter fractions than the feed oil are obtained, and the actual catalyst and operating conditions are selected so that fractions with a boiling point of 300°C or lower, particularly 125°C to 300°C, are obtained at a yield of 50% or higher.

The catalyst that is used is formed by supporting a hydrogenation active metal component, etc., on a carrier consisting of porous refractory material. Alumina, boria-alumina, silica-alumina, silica-titania, silica-zirconia, silica-magnesia, silica-alumina-titania, silica-alumina-zirconia, and their mixtures, as well as compound oxides of zeolite mixed with these are preferred as the carrier. In addition, a metal from Group 6, Group 9 or Group 10 of the Periodic Table is preferably used for the hydrogenation active metal component and actually, tungsten, molybdenum, nickel, cobalt, etc., can be used. Combination of tungsten or molybdenum and nickel or cobalt is particularly preferred. It is preferred that the total weight of

metal per catalyst weight of these metal components that is used be 1 to 35 wt%, particularly 5 to 30 wt%.

The organic nitrogen compound used in the present invention is an organic nitrogen compound whose boiling point is lower than the 50% distillation temperature of the starting material, particularly lower than  $(50\% \text{ distillation temperature } (^{\circ}\text{C})) \times (0.9)$  and exceeds  $200^{\circ}\text{C}$ , or a nitrogen compound contained in petroleum fractions whose 95% distillation temperature is lower than the 50% distillation temperature of the feed oil, particularly lower than  $(50\% \text{ distillation temperature } (^{\circ}\text{C})) \times (0.9)$ , and exceeds  $200^{\circ}\text{C}$ . Organic nitrogen compounds such as amines, pyridine, quinoline, indole, carbazole, etc., can be given as actual examples. Furthermore, derivatives of these organic nitrogen compounds and derivatives of other organic nitrogen compounds whose boiling point exceed  $200^{\circ}\text{C}$ , such as aniline derivatives, can be used.

The amount of organic nitrogen compound contained in the hydrogenation catalyst of the present invention is 0.01% or higher, preferably 0.1% to 1% in particular, in terms of the nitrogen weight. Because the organic nitrogen compound used by the present invention has the above-mentioned boiling point range and is contacted with catalyst before the hydrocracking process, the amount added can be very little when compared to conventional nitrogen compound additives.

The organic nitrogen compound can be added during catalyst production, but it is also possible to contact the nitrogen compound with the catalyst after the catalyst is loaded into the reactor so that the catalyst will contain the nitrogen compound. The organic nitrogen compound can be efficiently contacted with the catalyst after it has been loaded in the reactor by a process of bringing catalyst and organic nitrogen compound into contact prior to hydrocracking, for instance, during pre-sulfiding treatment. Furthermore, it is also possible to contact the organic nitrogen compound with the catalyst prior to the hydrocracking process, and thereafter to add nitrogen compound to the reactor during the hydrocracking process. In this case, the nitrogen compound can be mixed in the feed oil that serves as the starting material of the hydrocracking reaction, or it can be mixed in gas, such as hydrogen, etc., that will be introduced to the reactor. The nitrogen compound added to the hydrocracking reaction acts as a catalyst deactivation inhibitor, and in addition to the above-mentioned organic nitrogen compounds, can be ammonia or another nitrogen compound.

The organic nitrogen compound used in the present invention can be used as a compound alone, but it is simpler to use the organic nitrogen compound contained in the petroleum fraction. Actually, kerosene, gas oils, etc., that are ordinarily marketed can be used, and it is preferred that one whose nitrogen content

has been reduced to 2 to 200 ppm, preferably 2 to 100 ppm, particularly 10 to 100 ppm by hydrorefining be used. It is possible to bring the catalyst into contact with a solution of sulfiding agent dissolved in a solvent such as kerosene, gas oil, etc., and perform sulfiding so that organic nitrogen compound will be contained in the catalyst as a result of the sulfiding. Carbon disulfide, dimethyl sulfide, dimethyl disulfide, etc., can be used as the sulfiding agent.

#### EXAMPLES

Examples of contacting catalyst loaded in second-stage reactor 45 with an organic nitrogen compound when kerosene or gas oil fraction is to be produced by two-stage hydrocracking using the system shown in Fig. 4 with vacuum gas oil as the feed oil are described below.

##### Example 1

The feed oil fed to first-stage reactor 41 of the two-stage hydrocracking system is petroleum fraction with a boiling point range of 300 to 540°C and a nitrogen concentration 800 ppm. The product oil obtained from first-stage reactor 41 is distilled by distillation tower 43 and the fraction from the bottom of distillation tower 43 becomes the feed oil (recycle oil) of second-stage reactor 45. The product oil of second-stage reactor

45 and the product oil of first-stage reactor 41 are mixed and fed to distillation tower 43. The feed oil of this second-stage reactor 45 has a boiling point range of 290°C - 540°C and a nitrogen concentration of 1 ppm. The catalyst was hydrocracking catalyst comprising a nickel and a tungsten metal component on a silica-alumina carrier for both the first-stage and the second-stage reactor.

Prior to hydrocracking, pre-sulfiding of the catalyst loaded in second-stage reactor 45 was performed by passing gas oil (boiling point of 250 to 360°C) to which 1 wt% carbon disulfide had been added as the sulfiding agent through second-stage reactor 45. The sulfur concentration of the gas oil was 400 ppm and the nitrogen concentration was 50 ppm. Of these, it was shown that the gas oil contained 17 ppm acidic nitrogen compounds which are indole and carbazole derivatives and 16 ppm basic nitrogen compounds which are aniline, pyridine, and quinoline derivatives.

The time for which the gas oil was passed through the reactor during pre-sulfiding was adjusted so that the concentration of nitrogen adsorbed on the catalyst in second-stage reactor 45 would be 0.4% (nitrogen weight / loaded catalyst (fresh catalyst) weight).

Once pre-sulfiding was completed, operation of the system in Fig. 4 was switched to a two-stage hydrocracking operation and

hydrocracking was started. The hydrocracking operation lasted for 620 hours. It was found that the initial deactivation rate is 0.5°C/month or less. It was necessary to bring the reaction temperature of second-stage reactor 45 to 377°C in order to keep the conversion of fractions of 290°C or higher at 95 vol% after initial deactivation. The yield of middle distillates (130 to 290°C) was 66% (middle distillate weight/feed oil weight).

#### Example 2

Hydrocracking without recycling was performed using a system equipped with a one-stage reactor as shown in Fig. 1 with petroleum fraction with a nitrogen concentration of 1 ppm and a boiling point range of 290 to 540°C serving as the starting materials. The catalyst was hydrocracking catalyst comprising nickel and tungsten metal components supported on a silica-alumina carrier.

Pre-sulfiding of the catalyst was performed prior to hydrocracking by passing gas oil (boiling point range of 250°C to 360°C) to which 1 wt% carbon disulfide had been added as sulfiding agent through the reactor loaded with catalyst. The sulfur concentration of the gas oil was 400 ppm and the nitrogen concentration was 50 ppm. The time for which the gas oil was passed through the reactor was adjusted during sulfiding so that the nitrogen concentration adsorbed on the catalyst in the

reactor would be 0.4 % (nitrogen weight/loaded catalyst (fresh catalyst) weight).

When hydrocracking was started at a constant reaction temperature of 380°C once pre-sulfiding was completed, the conversion of fraction of 290°C or higher was 56% and the yield of middle distillates (130 to 290°C) was 38%.

#### Example 3

Other than the fact that 1% zeolite added to the carrier was used as the catalyst in the second-stage reactor, pre-sulfiding treatment of the catalyst and hydrocracking were performed under the same conditions as in Example 1. The reaction temperature of the second-stage reactor with which the conversion of fractions of 290°C or higher is 95 vol% was 377°C. The yield of middle distillates (130 to 290°C) was 64%.

#### Example 4

Tert-butyl amine (catalyst deactivation inhibitor) was mixed at 0.3 ppm in terms of the nitrogen concentration to feed oil in the second-stage reactor during the hydrocracking operation in Example 3. The reaction temperature of the second-stage reactor with which the conversion of fraction of 290°C or higher is 95 vol% was 379°C (2°C higher than in Example 1). The yield of middle distillates (130 to 290°C) was 67%.

### Example 5

Other than the fact that 10 ppm tert-butyl amine (catalyst deactivation inhibitor) in terms of the nitrogen concentration were mixed with the feed oil in the second-stage reactor, hydrocracking was performed as in Example 4. The temperature of the second-stage reactor at which the conversion of fraction of 290°C or higher is 95 vol% was 390°C. The yield of middle distillates (130 to 290°C) was 67%.

### Comparative Example

Other than the fact that the gas oil used for pre-sulfiding was changed to gas oil with a nitrogen concentration of 1 ppm, hydrocracking was performed under the same conditions as in Example 1. The concentration of nitrogen adsorbed on the catalyst in second-stage reactor 45 after pre-sulfiding was 0.003% (nitrogen weight/loaded catalyst (fresh catalyst) weight).

The initial deactivation rate when hydrocracking was started as in Example 1 was 2°C/day. It was necessary to keep the temperature of second-stage reactor 45 at 384°C in order to keep the conversion of fractions of 290°C or higher at 95 vol% after the initial deactivation. The yield of middle distillates was 65.4% (middle distillate weight/feed oil weight). When compared to Example 1, it is found that there is little nitrogen treatment

of the catalyst, the initial deactivation speed is high, activity after initial deactivation is over is low, and the middle distillate yield is low.

#### INDUSTRIAL APPLICABILITY

As previously described, according to the invention, hydrocracking catalyst was poisoned by an organic nitrogen compound with a boiling point that is lower than the 50% distillation temperature of the feed oil and that is 200°C or higher, or by the nitrogen compound contained in petroleum fractions having a 95% distillation temperature that is lower than the 50% distillation temperature of the feed oil, and as a result, it was possible to slow the initial deactivation rate of the hydrocracking catalyst and improve activity after the initial deactivation, and further, to improve middle distillate yield. As a result, hydrocracking can be efficiently performed for a long period of time.

## CLAIMS

1. A method of hydrocracking hydrocarbon oils, comprising the steps of:

pre-contacting a hydrocracking catalyst with an organic nitrogen compound; and

contacting a feed oil substantially comprised of hydrocarbon oils and hydrogen with the hydrocracking catalyst that has been contacted with the organic nitrogen compound in order to obtain a hydrocarbon oil with a lower boiling point than that of the feed oil;

the organic nitrogen compound being an organic nitrogen compound having a boiling point that is lower than a 50% distillation temperature of the feed oil and that is higher than 200°C.

2. A method of hydrocracking hydrocarbon oils derived from petroleum comprising the steps of:

contacting a petroleum fraction containing an organic nitrogen compound and having a 95% distillation temperature that is lower than the 50% distillation temperature of a feed oil substantially comprised of hydrocarbon oils and that is higher than 200°C with a hydrocracking catalyst; and

contacting the feed oil and hydrogen with the hydrocracking catalyst that has been contacted with the petroleum fraction in order to obtain a hydrocarbon oil with a boiling point lower than that of the feed oil.

3. The hydrocracking method according to Claim 1, further comprising a step of sulfiding the hydrocracking catalyst, wherein the step of contacting the organic nitrogen compound with hydrocracking catalyst and the step of sulfiding the hydrocracking catalyst are performed simultaneously.

4. The hydrocracking method according to Claim 2, further comprising a step of sulfiding the hydrocracking catalyst, wherein the step of contacting petroleum fraction with hydrocracking catalyst and the step of sulfiding the hydrocracking catalyst are performed simultaneously.

5. The hydrocracking method according to Claim 2, wherein the petroleum fraction comprises at least 2 ppm of the organic nitrogen compound by nitrogen weight.

6. The hydrocracking method according to Claim 1 or Claim 3, wherein, as a result of contacting the organic nitrogen compound with hydrocracking catalyst, the hydrocracking catalyst

comprises 0.01% to 1% by nitrogen weight of the organic nitrogen compound per catalyst weight.

7. The hydrocracking method according to any one of Claims 2, 4, and 5, wherein, as a result of contacting the petroleum fraction with hydrocracking catalyst, the hydrocracking catalyst contains 0.01% to 1% by nitrogen weight of the organic nitrogen compound per catalyst weight.

8. The hydrocracking method according to Claim 1 or 2, wherein a catalyst deactivation inhibitor is added when the feed oil and hydrogen are contacted with the hydrocracking catalyst.

9. The hydrocracking method according to Claim 8, wherein the catalyst deactivation inhibitor is a nitrogen compound.

10. The hydrocracking method according to Claim 9, wherein the inhibitor is added 5 ppm or less by weight of nitrogen per the feed oil.

11. The hydrocracking method according to any one of Claims 2, 4 and 5, wherein the petroleum fraction is gas oil.

12. A hydrocracking catalyst, which is used for hydrocracking a feed oil derived from petroleum by contacting the

feed oil and hydrogen with the hydrocracking catalyst to obtain a hydrocarbon oil with a boiling point lower than that of the feed oil, comprising:

a carrier made from a porous refractory oxide;

a hydrogenation active metal component, and

an organic nitrogen compound with a boiling point that is lower than the 50% distillation temperature of the feed oil and that is higher than 200°C,

the content of the organic nitrogen compound being not less than 0.01 wt% by nitrogen weight per the hydrogenation catalyst.

13. The hydrocracking catalyst according to Claim 12, wherein the organic compound is an organic compound contained in gas oil or kerosene.

14. The hydrocracking catalyst according to Claim 12 or Claim 13, which is produced by contacting a solution of sulfiding agent dissolved in gas oil or kerosene with the catalyst having the carrier and the hydrogenation active metal component.

FIG. 1

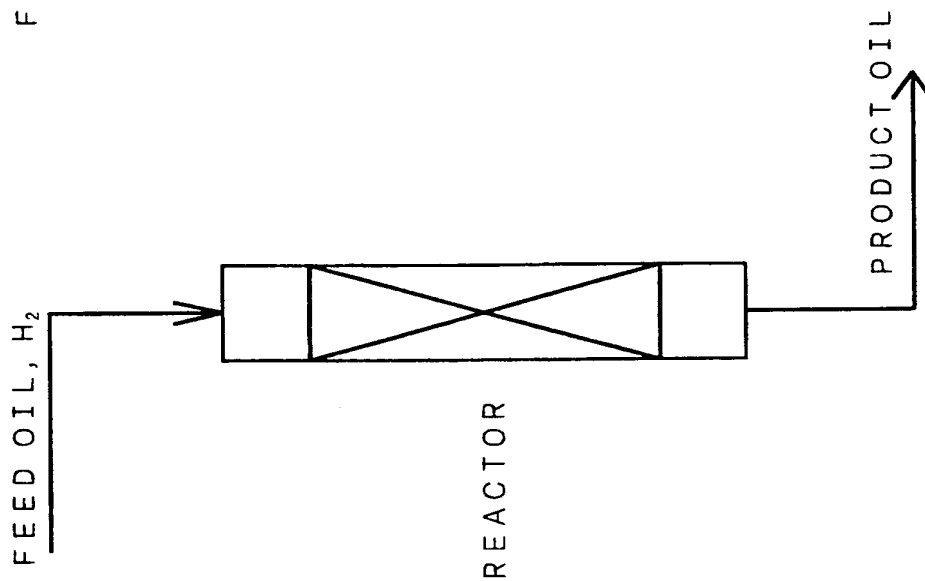


FIG. 2

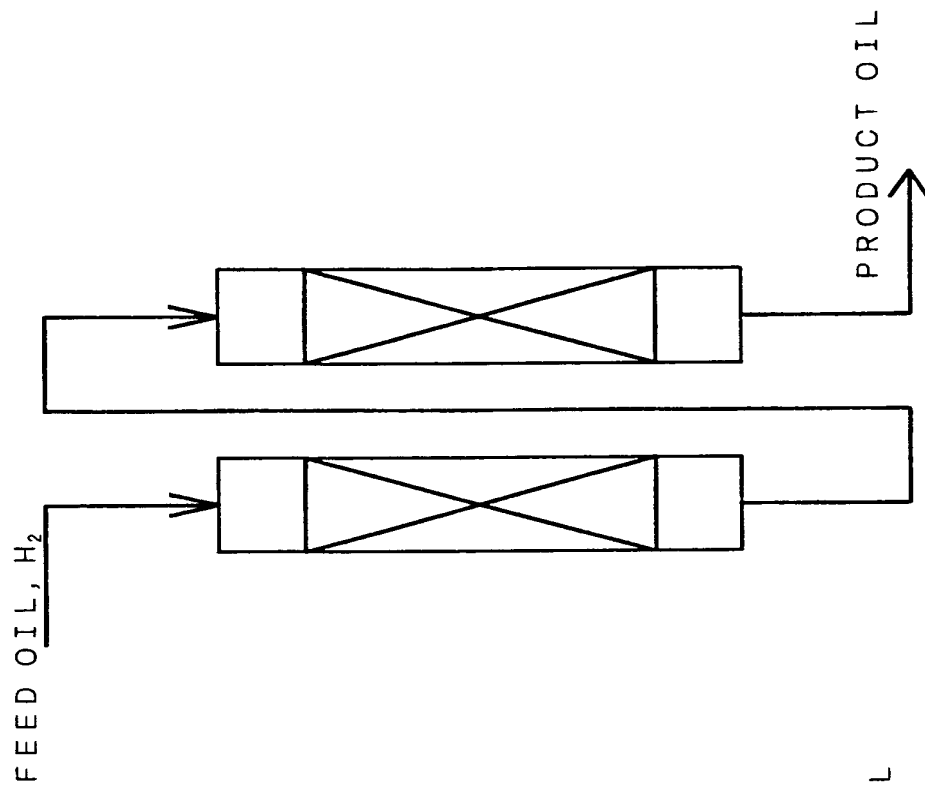


FIG. 4

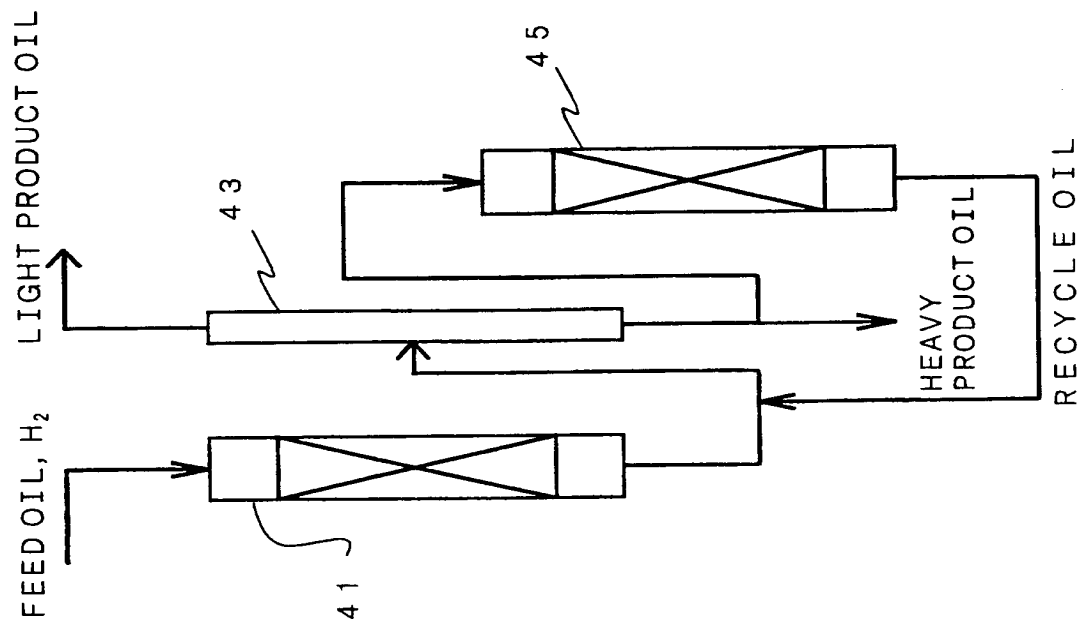


FIG. 3

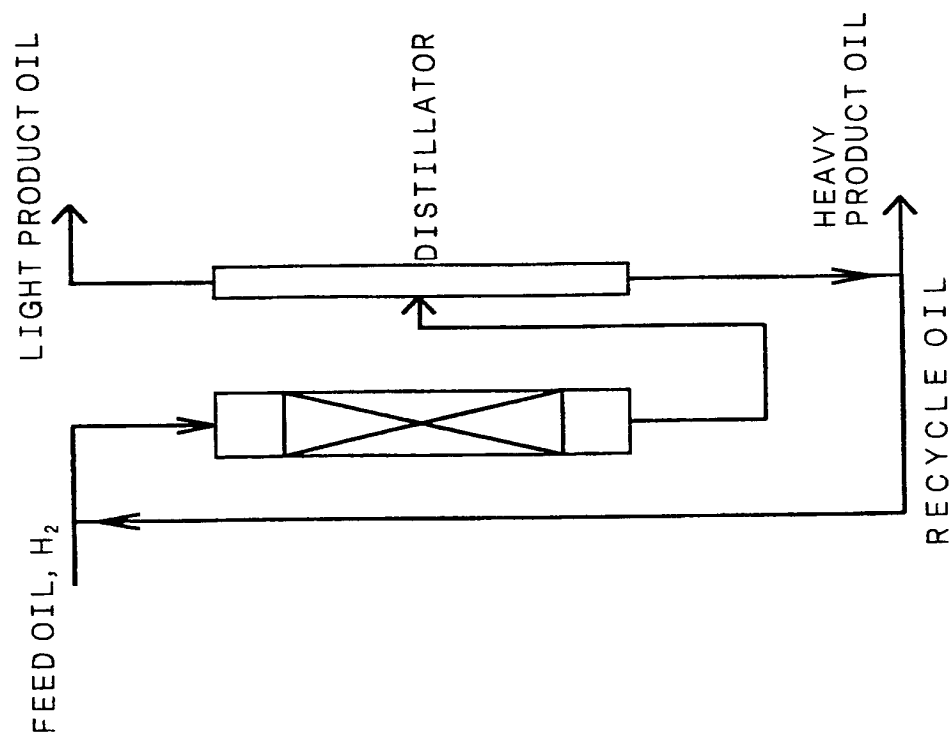


FIG. 5

